1,4-Dioxane Formation, Control, and Occurrence in Cleaning Products

August 21, 2019

Outline

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Quick Intro to ACI

- Founded in 1926, based in DC
- 140+ member companies
- Members include:
  - Manufacturers of household, I&I, healthcare cleaning products
  - Chemical producers (surfactants, fragrance, enzymes, etc.)
  - Finished packaging suppliers
  - Chemical distributors

american cleaning institute®
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A Snapshot of ACI Members

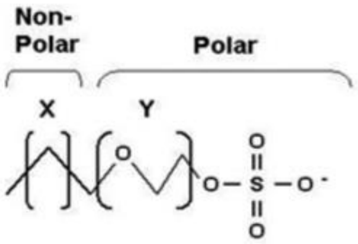
- BASF We create chemistry
- BRADFORD
- Church & Dwight Co., Inc.
- Corbion Keep creating
- CRODA
- DOW
- DUPONT
- EASTMAN
- ECOLAB
- Elevance Renewable Sciences
- EVONIK Power to create
- Firmenich
- Givaudan
- GOJO
- Henkel
- HUNTSMAN Enriching lives through innovation
- IFF
- innospec Touching Everyday Lives
- Lonza
- Lubrizol
- kuraray MonoSol
- novozymes
- OXITENO Evolution by chemistry
- P&G
- rb Health • Hygiene • Home
- SC Johnson A Family Company
- seventh generation
- Shell
- SOLVAY
- Stepan
- symrise

Surfactants

- Surfactants (surface active agents) are compounds that lower the surface tension (or interfacial tension) between two liquids, between a gas and a liquid, or between a liquid and a solid. Surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, and dispersants.
- Vital role in modern society – keeping consumers, our homes, workplaces, and public places, clean and sanitary.
  - Without surfactants many essential products would not exist: examples: laundry detergent, surface cleaners (kitchen, bathroom etc.), dish soaps, oven cleaners, body washes, shampoo etc.

There are two key classes of ethoxylated surfactants

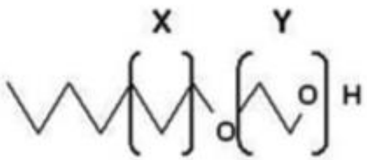
- Alcohol (Alkyl) Ethoxy Sulfate (ANIONIC SURFACTANT)



X = 10-13
(total alkyl length = C12-15)
Y (ethoxylates) = 0-6

$C_nH_{2n}\ (C_2H_4O)_mSO_4X$
$n = 12–18$
$m = 0–8$
X = sodium, ammonium or TEA

- Alcohol (Alkyl) Ethoxylate (NONIONIC SURFACTANT)



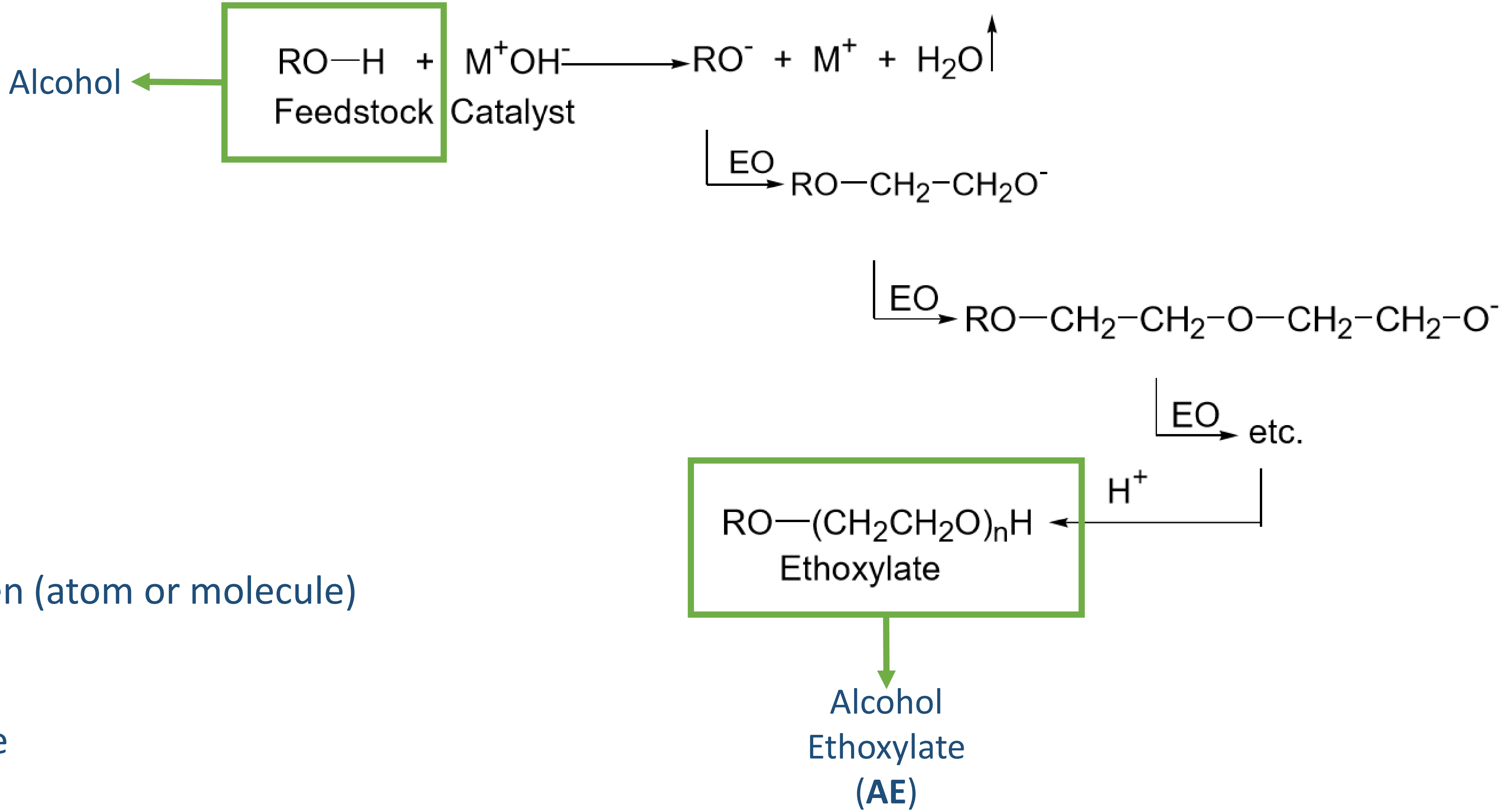
X = 6-12
(total alkyl length = C12-18)
Y (ethoxylates) = 0-18

C_nAE_m
$n = 8–18$
$m = 3–12$
A = alcohol
E = ethylene oxide

Ethoxylation and Sulfation

Ethoxylation

The process of reacting an alcohol with Ethylene Oxide to create an Ethoxylate/Alcohol Ethoxylate (non-ionic surfactant).



Where:

R = Carbon or Hydrogen (atom or molecule)

M^+= Molecular ion

EO = Ethylene Oxide

AE= Alcohol Ethoxylate

SO_3 Sulfation of AE $\Rightarrow$ AES

The process of reacting AE (nonionic surfactant) with Sulfur Trioxide to create an Alcohol (alkyl) Ethoxysulfate (anionic surfactant).

Alcohol Ethoxylate

$$\boxed{R\text{-}(EO)_n\text{-}OH} + SO_3 \longrightarrow \boxed{R\text{-}(EO)_n\text{-}OSO_3H} + \text{Byproduct}$$

Alcohol Ethoxysulfate (AES)

Where:

R = Carbon or Hydrogen (atom or molecule)

EO = Ethylene Oxide

AE = Alcohol Ethoxylate

AES = Alcohol Ethoxysulfate

SO_3 = Sulfur trioxide

Attributes Compared to Non-ethoxylayted Surfactants

Alkyl Ethoxysulfates

- Mass efficiency
- Better cleaning
- Better hardness tolerance
- Good for cold water
- Better for solubility/compaction
- Lower solvent requirement
- Good for grass cleaning
- Good for sebum cleaning
- Enzyme Stability
- Very high foaming

Alkyl Ethoxylates

- Mass efficiency
- Better hardness tolerance
- Better for solubility/compaction
- No solvent requirement in several formulations
- Good for grass cleaning
- Good for sebum cleaning
- Low foaming
- Mildness
- Enzyme stability

Comparison of Cleaning Power Between Alcohol Ethoxylates or Methyl Ester Ethoxylates Having Different EO Chain Lengths and a Common Anionic Surfactant

Yu Nagai1, Natsumi Togawa2 , Yumiko Tagawa3 and Keiko Gotoh2

Tenside Surf. Det. 51 (2014) 2 ª

“Ethoxylated nonionic surfactant in laundry detergents is mostly biodegradable alcohol ethoxylates (AE), which can remove sebum efficiently at low temperature [3 – 6]. AE can maintain enzyme stability in the presence of anionic surfactant [7] and therefore has excellent compatibility with enzyme in laundry detergents. [8].”

Other references citing the attributes of ethoxylated surfactants

DETERGENTS

Hendrik Hellmuth and Michael Dreja

Understanding Interactions of Surfactants and Enzymes: Impact of Individual Surfactants on Stability and Wash Performance of Protease Enzyme in Detergents

ORIGINAL ARTICLE

Synergism and Performance Optimization in Liquid Detergents Containing Binary Mixtures of Anionic–Nonionic, and Anionic–Cationic Surfactants

Nazanin Jadidi · Behrooz Adib · Farrokh B. Malihi

Received: 16 July 2011 / Accepted: 18 May 2012 / Published online: 24 June 2012

Environmental Attributes of Ethoxylated Surfactants

- Rapid and ultimate biodegradation
- 83.5-99.8% removal in WWTP
- No adverse impacts on the aquatic or sediment environments

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DOI: 10.1080/10739149.2013.803777

Environmental Safety of the Use of Major Surfactant Classes in North America

CHRISTINA COWAN-ELLSBERRY,[1] SCOTT BELANGER,[2] PHILIP DORN,[3] SCOTT DYER,[2] DREW McAVOY,[4] HANS SANDERSON,[5] DONALD VERSTEEG,[2] DARCI FERRER,[6] and KATHLEEN STANTON[6]
[1]*CE[2] Consulting, LLC, Cincinnati, OH, USA*
[2]*The Procter & Gamble Company, Mason, OH, USA*
[3]*Shell Health Americas, Houston, TX, USA*
[4]*University of Cincinnati, Cincinnati, OH, USA*
[5]*Aarhus University, Roskilde, Denmark*
[6]*American Cleaning Institute, Washington, DC, USA*

Significance of Attributes of Ethoxylated (nonionic) and Sulfated (anionic) Ingredients

- Multiple performance benefits, formulation versatility
- Human and environmental safety profile
- Holistic sustainability benefits

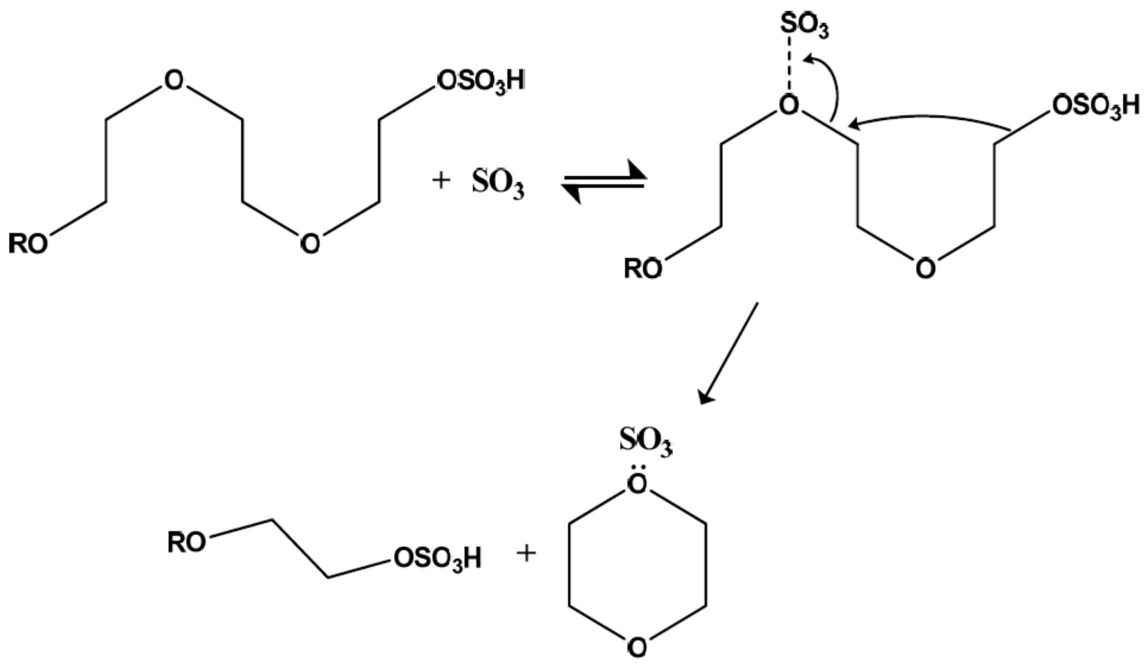
Formation of 1,4-Dioxane

Why is 1,4-Dioxane found at low levels in AE and AES surfactants?

- 1,4-Dioxane is not intentionally added, or used as a raw material in production

- It is a trace level **technically unavoidable** byproduct (impurity) from the chemical reaction itself

Byproduct of Sulfation: 1,4-Dioxane



1,4-Dioxane can be formed from ethoxymers with >1 mole of EO when excess SO_3 is used.

Where:
SO_3 = Sulfur Trioxide

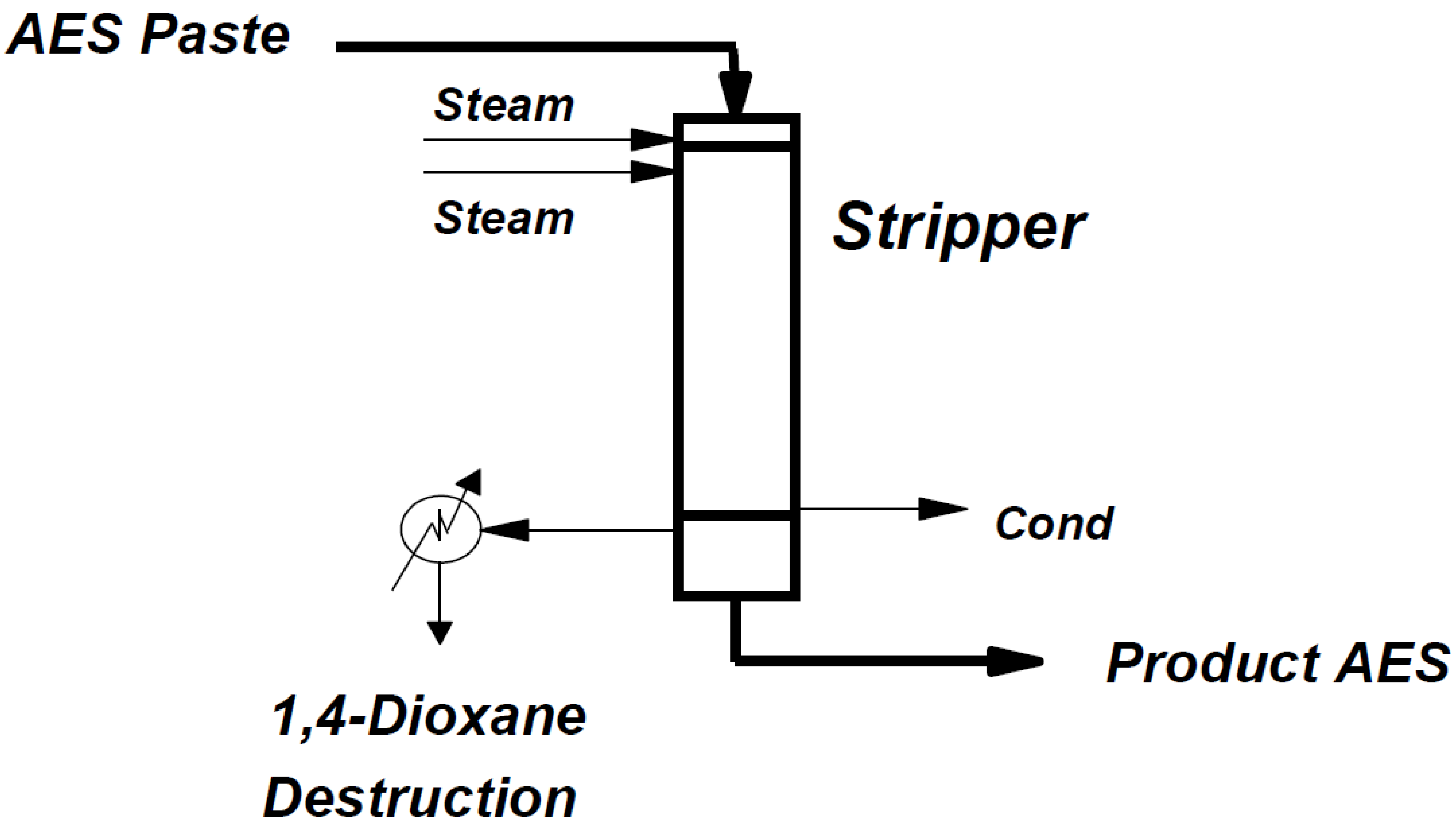
If $\frac{mols\ SO_3}{mols\ feedstock}$ > 1.04 then rapid increase in 1,4-Dioxane (Foster, 1997)

Control/Remediation of 1,4-Dioxane in Cleaning Product Ingredients

Control of 1,4-Dioxane During Sulfation of AE $\longrightarrow$ AES

- Process and Equipment Factors
  - SO_3: AE feed mole ratio
  - Reactor Loading
  - Residence time of AES acid prior to neutralization
- Feedstock Composition Factors
  - Average degree of ethoxylation
  - PEG and moisture content
  - EO adduct distribution

Remediation Mechanism – Stripping AES Paste



Occurrence of Ethoxylated/Sulfated Ingredients in Cleaning Products

Inventory of Cleaning Product Ingredients/Categories

- 57 ethoxylated ingredients in cleaning products
- All product categories contain ethoxylated ingredients
  - All Purpose Cleaners
  - Dish Care Products
  - Laundry Care Products

Measuring 1,4-Dioxane in Finished Products

- DTSC proposed EPA methods 8260 and 8270 use Flame Ionization Detection (FID) which is not considered very sensitive
  - Methods will measure to 2 ppm in liquid products without extraction, and down to 0.02 ppm with solid phase extractions, however, this approach may be problematic for cleaning products
  - Require time consuming steps and special equipment (steam distillation apparatus or purge and trap system)
  - More applicable for surface and drinking water and raw materials
- These limitations with current EPA analytical methods suggest there will be analytical challenges with more complex product matrices
- ACI and its members are partnering to advance and make available an aligned, robust and accurate quantitative method for 1,4-Dioxane in consumer products

Further Method Considerations

- Recent publications with personal care and cleaning products reference the use of 1,4 dioxane-d_8 as an internal standard:
    - Zhou, W. **2019** The Determination of 1,4-Dioxane in Cosmetic Products by Gas Chromatography with Tandem Mass Spectrometry. *Journal of Chromatography A* 460400 (FDA paper)
    - Shin, H.; Lim, H. **2011** Determination of 1,4-Dioxane in Water by Isotopic Dilution Headspace GC–MS. *Chromatographia,* 1233–1236
    - Sun, M.; Lopez-Velandia, C.; Knappe, D. **2016** Determination of 1,4-Dioxane in the Cape Fear River Watershed by Heated Purge-and-Trap Preconcentration and Gas Chromatography−Mass Spectrometry. *Environ. Sci. Technol*. 2246−2254
- Use of deuterated internal standard approach provides a simple, robust method that could be used by contract labs, avoiding the need for special equipment or high-end capability in a formulation setting for testing of finished products
- Additional considerations needed for manufacturing facilities
- Regardless of end-user, standard method development, validation, round robin testing for aligned industry approach requires attention

Environmental Monitoring Data

- 1,4-Dioxane is reported to be present in WWTP effluents at mean concentrations of ~1 ppb in the US (Simonich et al., 2013), and ~1 ppb in CA influents (DTSC AAT proposal, 2019)
- CA tap water levels are reported to range from <0.05 to 5.83 ppb (EWG National Tap Water Database)
- **Probability is negligible that dioxane inputs from upstream WWTPs result in intake concentrations exceeding the USEPA drinking water advisory concentration of 0.35 µg/L, before any treatment of the water for drinking use (Simonich et al., 2013)**

Thank you for your attention!

Kathleen Stanton

Senior Director, Technical & Regulatory Affairs

kstanton@cleaninginstitute.org